

## **MODIFICATION OF FERRIERITE CATALYSTS BY AQUEOUS TREATMENT**

### **FIELD OF THE INVENTION**

[0001] The present invention is directed at a method for improving isomerization properties of ferrierite catalysts. More particularly, the isomerization properties are improved by the use of an aqueous method treatment.

### **BACKGROUND OF THE INVENTION**

[0002] The use of steamed or water treated catalysts in isomerization processes is described in the art and literature. United States Patent Number 4,418,235 discloses the use of zeolites with a pore dimension greater than about 5 Angstroms, preferably 10-membered rings, with a silica to alumina ratio of at least 12 and a constraint index of about 1 to about 12. These zeolites undergo a treatment with steam or water prior to use and are used in an acid catalyzed conversion process.

[0003] United States Patent Number 4,374,296 discloses the use of zeolites with a pore dimension greater than about 5 Angstroms, preferably 10-membered rings, with a silica to alumina ratio of greater than 12 and a constraint index of about 1 to about 12. The catalysts undergo a controlled

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treatment to enhance the acidity, expressed as alpha, to about 300. These catalysts are used in the hydroisomerization of a C<sub>4</sub> to C<sub>8</sub> paraffin.

[0004] Other methods, which emulate the methods of United States Patent Number 3,293,192, have focused on severe treatments that target dealumination of the zeolite framework. While still other methods such as those reviewed by Kerr, *American Chemical Society Advanced Chemical Series*, vol. 121, 219 (1973) have targeted extraction of framework aluminum through the use of chemical extraction.

[0005] All of the above references are hereby incorporated by reference.

[0006] However, there still exists a need in the art for an improved isomerization catalyst.

#### **SUMMARY OF THE INVENTION:**

[0007] The present invention is directed at a method for treating a catalyst comprising ferrierite, or a zeolite isostructural to ferrierite, said method comprising:

- a) mixing said catalyst with an aqueous solution to form a slurry;

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- b) adjusting the pH of said aqueous solution to about 2 to about 7 by adding a reagent that does not have a deleterious effect on said catalyst;
- c) heating said slurry to a predetermined temperature between about 210°F to about 575°F (100 to about 300°C); and
- d) maintaining said slurry at said predetermined temperature for less than about 24 hours,

wherein after the above-described method, said catalyst shows removal of sorbed ammonia at a temperature about 248°F(120°C) lower than the same catalyst before the above-described method.

#### **DETAILED DESCRIPTION OF THE PRESENT INVENTION**

[0008] Ferrierite is a 10-ring mineral zeolite that is readily synthesized. Ferrierite is useful in many hydrocarbon conversion reactions such as cracking of low octane paraffins or selectively sorbing them. Ferrierite is also useful for converting linear paraffins to olefins and for the separation of single from multi-branched olefins and paraffins. Thus, it would be beneficial to improve the selectivity of ferrierite.

[0009] The present invention is a method of treating catalysts comprising ferrierite or zeolites isostructural to ferrierite such as, for example, FU-9, ISI-6,

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NU-23 and ZSM-35. The ferrierite catalysts are submerged in an aqueous solution having a pH of about 2 to about 7 at a predetermined temperature between about 210°F to about 575°F (100 to about 300°C) for a period of less than 24 hours. The present method does not target dealumination, and the ferrierite catalysts, after being effectively treated, do not show any evidence of dealumination. The ferrierite catalysts, after they have been subjected to the presently disclosed method, are typically referred to herein as aqueous-treated catalysts. Thus, "aqueous-treated", as used herein, is meant to refer to a catalyst that has been subjected to the presently disclosed aqueous catalyst treatment method prior to use. Untreated refers to a catalyst that has not been subjected to the presently disclosed aqueous treatment method.

[0010] As previously mentioned, ferrierite is generally considered a molecular sieve having the characteristics of a unidimensional 10 ring zeolite, i.e. a medium pore zeolite having unidimensional channels comprising 10 member rings. Zeolites are porous crystalline materials, and medium pore zeolites are generally defined as those having a pore size of about 5 to about 7 Angstroms, such that the zeolite freely sorbs molecules such as n-hexane, 3-methylpentane, benzene and p-xylene. Another common classification used for medium pore zeolites involves the Constraint Index test which is described in

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United States Patent Number 4,016,218, which is hereby incorporated by reference. Medium pore zeolites typically have a Constraint Index of about 1 to about 12, based on the zeolite alone without modifiers and prior to treatment to adjust the diffusivity of the catalyst.

[0011] Ferrierite can be readily synthesized, and the ferrierite catalysts used herein can be synthesized with or without a template. The templates used to synthesize ferrierite are typically organic in nature. Non-limiting examples of templates include tetramethylammonium, ethylenediamine, pyrrolidines, piperidines, etc. It is preferred that the ferrierite catalysts used herein be synthesized using an organic template.

[0012] It is also preferred that the ferrierite catalysts used herein contain at least one Group VIII metal, preferably a Group VIII noble metal, more preferably Pt and Pd, and most preferably Pt. The metals are present in an amount from about 0.05 to about 2.0 wt.%, preferably from about 0.1 to about 1.0 wt.%, based on the total weight of the catalyst. The metals can be incorporated through the use of any suitable means or technique known, such as, for example, incipient wetness.

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[0013] The present method involves an aqueous treatment wherein the ferrierite catalysts described above are submerged in an aqueous solution to form a slurry. The aqueous solution can be about 100% water or the aqueous solution can comprise water and a gas or other material that is substantially inert to the ferrierite catalysts. It is preferred that the aqueous solution be about 100% water, more preferably deionized water.

[0014] After the catalyst has been submerged in the aqueous solution, the pH of the slurry is adjusted. The pH can be adjusted through the use of any suitable conventional method or process. However, the pH is typically adjusted, or maintained, by the addition of a material that does not have a deleterious effect on the catalyst or the catalysts' functionality after the aqueous treatment. Preferably, an effective amount of an acid such as hydrochloric acid, preferably a dilute acid, is added to lower the pH of the slurry or an effective amount of a basic solution such as dilute aqueous ammonium hydroxide is added to raise the pH of the slurry. The pH of the slurry is adjusted to a desired pH in the range of about 2 to about 7, preferably to about 3 to about 5. Thus, by an effective amount of an acid or basic solution, it is meant that amount of acid or basic solution needed to adjust the pH of the aqueous solution to the desired pH.

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[0015] After the pH has been adjusted to the desired pH, the slurry is heated to a predetermined temperature, ranging from about 210°F to about 575°F (100 to about 300°C), preferably from about 284°F to about 500°F(140 to about 260°C), more preferably from about 355°F to about 428°F(180 to about 220°C). The catalyst is subjected to the aqueous treatment conditions for an effective amount of time, which is typically less than about 24 hours, preferably less than about 20 hours, and more preferably about 12 to about 18 hours. As previously stated, the present method does not target dealumination, and the ferrierite catalysts, after being effectively treated, do not show any evidence of dealumination.

[0016] By "effectively treated" it is meant that the resulting aqueous-treated catalyst is capable of desorbing sorbed ammonia at temperatures lower than the same untreated catalyst. Typically the aqueous-treated catalyst is capable of desorbing sorbed ammonia at temperatures about 248°F(120°C) lower than the untreated catalyst, preferably from about 76°F to about 248°F(80 to about 120°C) lower than the untreated catalysts, more preferably about 194°F to about 230°F(90 to about 110°C), and most preferably about 203°F to about 221°F(95 to about 105°C). The decrease in temperature at which sorbed

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ammonia is desorbed is accompanied by a reduction of catalytic acidity. Thus, the aqueous-treated catalyst has less of a tendency towards non-selective cracking and shows improved isomerization characteristics. Therefore, an effectively treated catalyst is one that demonstrates the desorption of sorbed ammonia at temperatures lower than an untreated catalyst, a decrease in tendency towards non-selective cracking, and improved isomerization characteristics. The reason for the improved desorption properties resulting from the aqueous treatment is unknown. However, the inventors hereof, while not wishing to be limited by theory, believe that changes in surface properties, structural annealing to eliminate structural defects or changes in metal dispersion, or combinations of these account for the aqueous-treated catalyst having a decreased tendency towards non-selective cracking, reduction of the temperature at which sorbed ammonia is removed, and improved isomerization characteristics.

[0017] Also, as previously stated, it is preferred that the catalysts used herein contain at least one Group VIII metal, preferably a Group VIII noble metal, and most preferably Pt. The at least one Group VIII metal can be added to the ferrierite catalysts before or after they have been subjected to the presently disclosed method. However, it is preferred that the ferrierite catalysts

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be subjected to the presently disclosed method subsequent to the incorporation of the at least one Group VIII metal.

[0018] The ferrierite catalysts can also be combined with a suitable porous binder or matrix material. Non-limiting examples of such materials include active and inactive materials such as clays, silica, and/or metal oxides such as alumina. Non-limiting examples of naturally occurring clays that can be composited include clays from the montmorillonite and kaolin families including the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia, and Florida clays. Others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite may also be used. The clays can be used in the raw state as originally mixed or subjected to calcination, acid treatment, or chemical modification prior to being combined with the ferrierite.

[0019] It is preferred that the porous matrix or binder material comprises silica, alumina, or a kaolin clay. It is more preferred that the binder material comprise alumina. In this embodiment the alumina is present in a ratio of less than about 15 parts ferrierite to one part binder, preferably less than about 10, more preferably less than about 5, and most preferably about 2.

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[0020] The use of the aqueous-treated catalysts typically improves the product selectivity of hydrocarbon conversion processes by more than about 20 percent, preferably more than about 30 percent, more preferably about 50 percent, and most preferably more than about 50%, as illustrated in the Examples below.

[0021] The above description is directed to one embodiment of the present invention. Those skilled in the art will recognize that other embodiments that are equally effective could be devised for carrying out the spirit of this invention.

[0022] The following examples will illustrate the improved effectiveness of ferrierite catalysts treated by the instant method, but are not meant to limit the present invention.

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## EXAMPLES

### EXAMPLE 1 (COMPARATIVE)

[0023] A base untreated ferrierite catalyst, Zeolyst (CBV-914B), having a Si/Al ratio of about 10 was obtained commercially. This catalyst was presumably made using an organic template, outlined in United States Patent Numbers 4,252,499 and 4,942,027. The untreated ferrierite was prepared by calcining to remove the template, ammonium exchanged, and exchanged with a solution of  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2\text{H}_2\text{O}$  to yield a catalyst having 0.5 wt.% Pt, based on the total weight of the catalyst. The untreated ferrierite exchanged catalyst was then calcined in air at 115°C, followed by a programmed calcination comprising heating for 30 minutes at 115°C, increasing the temperature at 0.5°C/minute to 450°C, then holding the temperature at 450°C for 2 hours. The catalyst was then cooled, pilled, ground, and sieved into particles ranging from about 0.85 to about 2.0mm for catalyst testing. The catalyst was dried for at least 30 minutes in a 250°C oven. A 0.50g portion of the dried ferrierite was then mixed with 5.0g of about 0.25-0.66mm quartz chips to form a catalyst charge. The catalyst charge was loaded into a 1cm diameter, stainless steel, downflow, automated reactor equipped with an on-line gas chromatogram containing a 50m capillary column. The ferrierite samples used herein were then pretreated by ramping the temperature to 150°C and holding that

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temperature for 30 minutes under a flow of 200 SCCM dry nitrogen. The nitrogen was switched to hydrogen and the temperature ramped to 350°C and held there for 60 minutes to reduce the platinum. The temperature was reduced to 240°C and hydrogen and decane were introduced at a rate of 29 WHSV(weight hourly space velocity), while a total pressure of 200psig and a H<sub>2</sub>:feed ratio of 10 were maintained. The temperature was increased in 20°C increments to a maximum of 400°C, and held at each increment for a period of 30 minutes. The conversion of decane was measured at each temperature, and the results are given in Table 1 below.

[0024] At a standard comparative temperature of 320°C, this untreated ferrierite catalyst converted 69% of the feed, wherein 24% were decane isomers and 41% were cracked products. In evaluating the temperature dependence of activity and selectivity, this was the maximum isomerization yield observed with this catalyst.

## EXAMPLE 2

[0025] A 5g sample of the untreated ferrierite catalyst was slurried in 50g of deionized water in a 125 Teflon autoclave liner (Parr 4748 acid digestion bomb). The pH was adjusted to 2 by adding dilute HCl, and the liner was

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capped and placed in the bomb container and sealed. The bomb was rotated at 12rpm in the presence of air in an air oven at 200°C and held at that temperature for about 18 hours. The bomb was then cooled, and the contents removed. The contents of the bomb were filtered to retrieve the ferrierite catalyst particles and the catalyst particles were washed with deionized water and dried at 115°C. The ferrierite catalyst was then prepared for testing and evaluated using the same catalytic procedure and preparation methods described in Example 1. The conversion of decane was measured, and the results are given in Table 1 below.

[0026] At a standard comparative temperature of 320°C, this treated ferrierite catalyst converted 23% of the feed, wherein 17% were decane isomers and 6% were cracked products. In this case, maximum isomerization was observed at 380°C with a conversion of 66% of the feed, wherein 39% were decane isomers and 27% cracked products. The activity of this catalyst has been moderated, but its selectivity to desired products has been enhanced compared to the base catalyst of Example 1.

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### EXAMPLE 3

[0027] A 5g sample of the base ferrierite catalyst from Example 1 was treated the same as the catalyst of Example 2, except that the pH was adjusted to 7 with a few drops of dilute aqueous ammonium hydroxide. The treated catalyst was subjected to the standard catalyst preparation and treatment procedures discussed in Examples 1 and 2.

[0028] At a standard comparative temperature of 320°C, this treated ferrierite catalyst converted 45% of the feed, wherein 29% were decane isomers and 16% were cracked products. In this case, maximum isomerization was observed at 340°C with a conversion of 61% of the feed, wherein 34% were decane isomers and 27% cracked products.

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[0029] Samples of ferrierite catalysts were prepared according to the procedure outlined in Examples 1, 2, and 3. However, the treatment temperature and pH was varied, as shown in the following Table 1.

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Table 1

Example #	Treatment	320°C Data			% Decane Isomers	Cracked Products	Temperature (°C)	% Decane Isomers	% Conversion	Selectivity	Data % Cracked Products
		% Conversion	% Decane Isomers	% Cracked Products							
1	T°C/pH NONE	69	24	41			320		27	69	41
2	200/2	23	17	6			380		39	66	27
3	200/7	45	29	16			340		34	61	27
4	165/4	50	32	18			340		37	66	30
5	165/5	48	37	11			340		45	65	20
6	165/2	38	29	9			360		42	67	24
7	240/4	21	18	3			380		45	68	20
8	200/3.4	34	25	9			360		42	70	25
9	200/3.6	32	26	6			360		45	60	16
10	200/5	50	40	10			360		48	76	27
11	200/3	33	26	8			360		42	62	20

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[0030] It is clear from the data contained in Table 1 that the controlled aqueous treatments between a pH of about 2 to about 7 in the temperature range of about 140 to about 260°C provides favorable activity and selectivity improvements over the prior art ferrierite catalysts, represented here by the commercial catalyst evaluated in Example 1. As can be seen from the data contained in Table 1, optimized performance of the water-treated ferrierite catalysts is achieved in the preferred pH range of between about 3 and 5, and over the more preferred temperature range of between about 180 to about 220°C.